

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> B03B 1/04, B03D 1/12, 1/02 B03B 9/00, C04B 33/04 B28C 1/08	<b>A1</b>	<b>(11) International Publication Number:</b> WO 93/00999 <b>(43) International Publication Date:</b> 21 January 1993 (21.01.93)
<b>(21) International Application Number:</b> PCT/US92/05182 <b>(22) International Filing Date:</b> 16 June 1992 (16.06.92)  <b>(30) Priority data:</b> 725,713                      3 July 1991 (03.07.91)                      US  <b>(71) Applicant:</b> ENGELHARD CORPORATION [US/US]; 101 Wood Avenue, Iselin, NJ 08830 (US).  <b>(72) Inventors:</b> GANTT, George, E. ; 200 Kenan Drive NW, Milledgeville, GA 31061 (US). ADKISSON, Thomas, J. ; 1490 Rivernorth Blvd., Macon, GA 31211 (US). GLADIN, Preston, B. ; 153 Honeysuckle Road, Mil- ledgeville, GA 31061 (US). USSERY, Randall, E., Jr. ; Rte. 1, Box 2095, Gordon, GA 31031 (US).		<b>(74) Agents:</b> MILLER, Stephen, I. et al.; Engelhard Corpora- tion, 101 Wood Avenue, Iselin, NH 08830 (US).  <b>(81) Designated States:</b> AU, BR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LU, MC, NL, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> SELECTIVE SEPARATION OF FINELY-DIVIDED MINERALS BY ADDITION OF SELECTIVE COLLEC- TOR REAGENT AND CENTRIFUGATION  <b>(57) Abstract</b>  Separation of impurities from kaolin clay is accomplished by conditioning a dispersed aqueous pulp of the clay with an an- ionic flotation collector, followed by centrifugation or the like to cause the impurities to settle from a dispersed pulp of the clay without an intermediate froth flotation step or a flotation waste froth is centrifuged or hydrocloned to recover valuable kaolin contained in the froth.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FI	Finland	ML	Mali
AU	Australia	FR	France	MN	Mongolia
BB	Barbados	GA	Gabon	MR	Mauritania
BE	Belgium	GB	United Kingdom	MW	Malawi
BF	Burkina Faso	GN	Guinea	NL	Netherlands
BG	Bulgaria	GR	Greece	NO	Norway
BJ	Benin	HU	Hungary	PL	Poland
BR	Brazil	IE	Ireland	RO	Romania
CA	Canada	IT	Italy	RU	Russian Federation
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark	MG	Madagascar		
ES	Spain				

5        SELECTIVE SEPARATION OF FINELY-DIVIDED MINERALS BY  
         ADDITION OF SELECTIVE COLLECTOR REAGENT  
         AND CENTRIFUGATION

10       1.    FIELD OF INVENTION

15       This invention relates to the separation of finely  
divided minerals from other finely-divided minerals in  
the presence of water which utilizes reagents of the type  
used in differential froth flotation but does not employ  
a frothing step and the use of flotation cells to effect  
the separation. The invention relates particularly to  
the separation of colored titaniferous impurities from  
impure kaolin clay which employs augmented gravitational  
forces instead of froth flotation to separate impurities  
from the kaolin.

20

2.    BACKGROUND OF THE INVENTION

25       Froth flotation has been practiced for over a  
century to separate mineral particles on the basis of  
differences in chemical composition. Early examples  
include the separation of sulfide minerals from oxide  
gangue by forming the ore into an aqueous pulp, adding a  
xanthate collector reagent which selectively coats one or  
more desired sulfide minerals from gangue, adding a  
frother, and subjecting the reagentized ore pulp to  
aeration by various means. A froth product which is a  
concentrate of the sulfide minerals which report as a  
froth which is then separated from the nonfloated gangue-  
rich aqueous pulp.

35       Froth flotation was most readily implemented when it  
was applied to sulfide minerals, especially those of  
relatively large particle size, for example, larger than  
10 microns. A subsequent development was the adaptation  
to the selective flotation of so-called "oxidized"

minerals such as cassiterite, fluorspar, scheelite and titania from other oxidized minerals using anionic (negatively charged) collectors, such as fatty acids or modified fatty acids, sometimes augmented by reagents to control selectivity and/or to control frothing. These processes were also more difficult to implement when the ore in the pulp was very finely mineralized or if the pulp contained slimes.

10 In all but the coarser particle size fractions of typical kaolin crudes, most of the particles are finer than 5 microns. In fact, the kaolin in the crudes usually have an average particle size (as determined by conventional sedimentation techniques) below 2 microns and frequently have a significant content of particles in the submicron-size range. Furthermore, the colored impurities (principally iron-fearing titanias) are present in small amounts, e.g., 1 - 5% of the weight of a degritted crude and in the form of very fine particles.

15 Thus one of the greatest challenges in the art of froth flotation was the selective flotation of colored impurities indigenous to most kaolin clays from the kaolin particles.

25 The successful large-scale flotation purification of kaolins awaited the development in the 1960's of so-called "Ultraflotation", U.S. 2,990,958, the teachings of which are incorporated herein by cross-reference. The process achieved the flotation of colored titaniferous impurities from fine particle-size fractions of kaolin crude by utilizing several modifications of conventional froth flotation technology, including the use of a clay dispersant anionic (mixture of fatty acids and rosin acids) addition of "auxiliary," or carrier, mineral particles (calcite) amenable to flotation with an anionic

30

35

collector, and oils to control frothing. In carrying out the process, the impurities and the calcite were selectively coated with the anionic collector. When the ore pulp was aerated these minerals reported in the froth which was separated on a continuous basis from the remainder, a dispersed pulp of purified kaolin was recovered. The purified clay was further processed by bleaching, filtration washing, etc. In preferred embodiment, the kaolin pulp was first degrittied to remove gross particles, generally larger than 325 mesh. Following this the degrittied pulp was separated into a fine and coarse particle size fraction, the fine fraction, for example a fraction 80% or 90% by weight finer than 2 microns, being the one which was "conditioned" with the collector and "carrier." The pulp thus conditioned was charged to the flotation cells where other reagents were added. A bank of flotation cells were used in the process, as is conventional in ore flotation, with the froth from one cell being diluted with water to facilitate transfer to the next cell, etc. and the machine discharge products (nonfloated material) being combined to maximize recovery of purified kaolin. The froth product was transferred to an appropriate waste disposal site.

25

Subsequent efforts to beneficiate kaolin clay by froth flotation include TREP, a flotation operation that can be applied to whole (unfractioned kaolin crudes) and can be operated at higher solids than Ultraflotation, TREP features the use of an oleic acid collector with a calcium salt such as calcium chloride in flotation cells in which air is introduced into a recycle stream of beneficiated clay. In this case, as in Ultraflotation, the concept of using an anionic organic collector for colored impurities such as titaniferous matter, followed

35

by aeration and flotation is applied. See U.S. 4,472,271, the teachings of which are incorporated here by cross-reference.

5           Another variant of the anionic froth flotation purification of kaolin clay is described in U.S. 3,979,282 which includes an example for the removal of colored tourmaline from a clay.

10           While many advances have been made in these schemes for removing colored impurities from kaolin clay, sometimes referred to as "china clay," most of the developments have adhered to the concept of using an anionic collector to selectively float impurities and  
15           aeration and flotation to effect the separation. Exceptions are high intensity magnetic separation procedures, now widely used in industry, frequently in combination with froth flotation. Also, schemes have been proposed to selectively flocculate impurities from  
20           kaolin or to selectively flocculate kaolin from impurities with high molecular weight charged polymers such as polyacrylamide, followed by physical separation of flocculated matter from dispersed particles. Also, it has been proposed to permit an anionically conditioned  
25           pulp of impure kaolin to settle quiescently, whereby aeration introduced during conditioning causes impurities to float on a pulp of purified clay. The floated impurities are skimmed from the surface of the pulp of purified kaolin. See U.S. 3,670,883.

30           None of these procedures has met the widespread acceptance of froth flotation and, in the case of magnetic purification, the technique does not remove titaniferous and other very weakly paramagnetic  
35           impurities to the extent achievable by froth flotation.

Thus, the froth flotation method for purifying kaolins is one of the largest commercial industrial mineral beneficiation operations in existence.

5        Froth flotation of kaolin is not without drawback, especially in the present industrial climate in which large scale industrial equipment such as float cells are expensive and wastage of valuable mineral resources through processing loss is of great commercial  
10        significance. Further, production of by-product waste streams must be minimized for environmental reasons. Thus, kaolin flotation as presently practiced, even in advanced modes, results in the recovery of beneficiated kaolin in the form of relatively dilute effluents,  
15        typically about 13 to 18% solids, depending upon grade, in the case of Ultraflotation and about 30 to 35% solids in the case of TREP. This means that water must be removed from the pulp of dispersed purified kaolin before further processing such as bleaching is carried out. It  
20        would be highly advantageous to achieve the high level of titania removal achievable by froth flotation while generating more concentrated streams of kaolin products. Among other obvious benefits, prolonged aging in settling tanks would be avoided, thus minimizing the amount of  
25        undesirable airborne quartz dust introduced into the clay during settling.

While there has been ongoing effort by practitioners of the technology to avoid losses of kaolin with the  
30        floated impurities, this has been unavoidable in large scale commercial operations. Thus, typical kaolin losses in Ultraflotation are about 8%, based on the weight of kaolin feed to the conditioners and are about 10% in TREP.

Kaolin products, especially premium grades such as those necessitating beneficiation, are supplied as grades, depending upon particle size and brightness criteria. Kaolin clays are polydispersed in the sense  
5 that the particles are not composed of particles of a single particle size. If they were, impurities could readily be separated from the kaolin by gravity, provided the impurities had different settling velocities. However, not only are kaolins composed of particles of  
10 widely different particle size ranges, e.g., particles as fine as 0.2 microns up to 10 microns, but the distribution of the impurities is such that Stokes law, as applied to gravity settling or even high speed centrifuges, will not separate titaniferous impurities in  
15 most kaolins to the extent achievable by froth flotation when applied to simple dispersed kaolin pulps. Thus, it is conventional practice to centrifuge kaolin feed before it is charged to flotation equipment, as in Ultraflotation, or after flotation, as in TREP to recover  
20 kaolin fractions of various sizes. The primary role of centrifugation in these operations is to produce grades of desired particle size and not primarily to purify the kaolin.

25 A related challenge to the kaolin industry is the physical recovery of valuable kaolin from a flotation waste before the waste is impounded in an environmentally acceptable manner. The kaolin should be recovered as a grade of desired particle size. This not only improves  
30 the recovery of valuable kaolin but reduces the volume of waste that must be handled. Waste includes titania and/or other impurities as well as organic and inorganic flotation reagents. In the case of Ultraflotation, the wastes also include substantial volumes of carrier  
35 (calcite) and other reagent used to float carrier and



impurity. For example, a calcite carrier is typically used in amount of about 12 to 20% based on the weight of kaolin flotation feed. The discarded froth product typically contains about 85 to 95% calcite. See U.S. 4,014,709. Early in the development of Ultraflotation a proposal was made to remove the calcite carrier from a kaolin froth product by adding a powerful dispersant (TSPP) to remove reagent from carrier. Although the process did place the carrier in reusable form, it removed collector, therefore necessitating further addition of flotation oil before the material could be reused in Ultraflotation. It would be desirable when treating such a waste by-product to recover the carrier without removing flotation reagents therefrom.

15

#### SUMMARY OF THE INVENTION

We have made the unexpected discovery that dispersed kaolin obtained by flotation purification with an anionic collector reagent selective to the flotation of colored impurities in the kaolin feed can be recovered from an aqueous waste froth product including anionically reagentized impurities and occluded kaolin by subjecting the waste to gravitational force in a centrifuge or hydroclone.

25

We have made the further unexpected discovery that a kaolin feed pulp reagentized with an anionic collector selective to froth flotation of colored impurities can be purified without aeration and flotation simply by subjecting the reagentized pulp to sufficient gravitational force, as in a centrifuge or hydroclone, to cause the impurities to settle, whereby the purified kaolin is recovered as an overflow product without dilution instead of as a diluted underflow product as it

35

is in froth flotation. A significant benefit, in addition to improved recovery of beneficiated kaolin product and reduced losses in the wastes, is the ability to recover the beneficiated kaolin without the need to use dilution water as required to transfer froth from cell to cell in conventional froth flotation. Further, the need to acquire, install and maintain flotation cells is avoided. The significance of being able to beneficiate without using flotation cells is best appreciated by the visitor to a flotation plant who observes the extensive capital expenditure and energy costs involved in large-scale froth flotation.

While the invention has been described with special reference to its utility in kaolin flotation, it is believed that the benefits will be realized with other flotation processes in which a finely mineralized ore pulp or a slimed pulp which is amenable to selective froth flotation in the presence of an appropriate collector. Nonlimiting examples are the flotation of carbonate (e.g., calcite, magnesite), cassiterite, scheelite, and fluorspar ores using a dispersed aqueous pulp with an anionic collector to float the valued minerals from silica and silicate gangue. Using the process of the invention, the reagentized mineral, e.g., carbonate, cassiterite, scheelite or fluorspar, may be recovered as a centrifuge (or hydroclone) underflow product instead of as a floating froth.

DESCRIPTION OF PREFERRED EMBODIMENTS

In one embodiment, the charge to a centrifuge or a hydroclone is a waste product from a froth flotation process for beneficiating kaolin clay wherein the froth contains water in which is suspended an agglomerated concentrate of colored impurities originally in the kaolin, including iron-bearing titania in the case of most Georgia kaolin, and in some cases including one or more iron minerals, mica or ilmenite or tourmaline. The impurity or impurities are coated with an anionic reagent. The waste also contains dispersed particles of kaolin clay. In the case of a froth product from an Ultraflotation process, the froth will include virtually all of the calcite or other "carrier" added in the process, the calcite also being coated with the collector. Typically the collector is oleic acid, or mixtures of oleic and rosin acids. However, other anionic collectors, such as, for example, hydroxyamates, linoleic acid or sulfonated fatty acids, may constitute all or part of the collector. Residual flotation oils, such as the fuel oil employed to control froth or a petroleum sulfonate salt such as used in Ultraflotation may be present in the froth product. Small amounts of water soluble reagents used or formed in the flotation process may also be present. These include one or more anionic dispersants, typically an alum-silica hydrosol, sodium silicate, sodium carbonate, sodium polyacrylate or mixtures thereof. Soluble material in the flotation process will be concentrated in the recovered dispersed pulp of purified kaolin. Reference is made to U.S. 4,014,729 for a disclosure of the composition of a typical Ultraflotation waste product.

Typically pH of the froth waste is alkaline, e.g.,

above 8. Solids are generally above 30% by weight and are frequently higher. The solids in the froth product, at least the collector-coated solids, are in agglomerated condition, whereby they can be separated from the kaolin  
5 by centrifugation or hydroclones which will not accomplish the same virtually quantitative separation of kaolin particles from impurities if all of the particles were dispersed, as they are in conventional processes for separating mineral mixtures into fractions based on  
10 particle size. In other words the presence of flotation collector is vital to the separation to be accomplished by the invention.

In practicing the other embodiment of the invention  
15 wherein a dispersed kaolin pulp is conditioned for froth flotation but, instead of purifying the conditioned pulp in flotation cells, the pulp is charged to one or a series of centrifuges or hydroclones. In this case, frothers and reagents intended primarily to serve as  
20 frothers or froth control agents need not be present in or added to the conditioned pulp.

The teachings of the above cross-referenced patents are illustrative of reagents that can be used to disperse  
25 kaolin pulps for froth flotation and reagents and other operating conditions that are useful in the conditioning step. These patents are also referenced for their disclosures of equipment useful in the conditioning step. See also U.S. 4,483,624. Those skilled in the art of  
30 froth flotation will recognize that in froth flotation, conditioning is a step distinctive from aeration and flotation. Thus, the purpose of conditioning is to distribute the collector in the aqueous mineral pulp so that it will selectively coat the mineral or minerals to  
35 be floated; conditioning is not intended to introduce air

-11-

bubbles, although minimal aeration during conditioning will not be detrimental. However, if formation of a strong tenacious froth occurs such as may be desired in froth flotation, this may not be desirable and is not essential.

In practice of the invention, the "G" force necessary in the operation of a centrifuge or the like can be determined by simple experimentation in which "G" is varied and the desired separation is observed. Ideally, the gravity separation will remove virtually all kaolin particles as a centrifuge (or hydroclone) overflow product and, therefore, the particle size distribution of the kaolin will be that of the feed kaolin in both embodiments of the invention. Obviously, insufficient gravitational force will not effectively separate kaolin from other materials, and excessive force will cause all solids to deposit as a solid.

The following examples are given for illustrative purposes and are not to be construed as limiting the invention unless otherwise indicated.

Conditioning for Ultraflotation, referred to in the following illustrative examples, was conducted in ten conditioning cells, 9.5 feet high, 8 foot diameter, equipped with 200 horsepower, 880 RPM agitators. Also used were three preconditioners, 5 x 5 foot, 5 horse motors, 1800 RPMs. Ultraflotation is carried out using sixty-eight Denver Model H5854A flotation cells with 20 horsepower 800 RPM motors. Utilization of this equipment includes sixteen rougher cells, twelve first cleaning cells, eight second cleaning cells, eight third cleaning cells, twelve recovery cells, and twelve refloat cells.

-12-

Additional horsepower includes the recovery froth conditioner, 200 horsepower and the rougher froth conditioner, 200 horsepower. Other horsepower is required for pumps, paddles, etc.

5

Conditioning for TREP was carried out in a squirrel cage conditioner, described in U.S. 4,483,624.

10       Fractionation gravity separation equipment utilized in the following illustrative examples includes a Damon Model CU-5000 laboratory centrifuge which is capable of operating up to 6000 G's. Fractionation for experimental purposes was maintained at approximately 800 G's. Pilot scale fractionation was accomplished utilizing a Sharples  
15       solid bowl centrifuge, Pilot Plant size Type BM357A-10A, Serial No. 55P4486, capable of a maximum rotational speed of 4000 RPMs. Fractionation utilizing this equipment was controlled to simulate approximately 1200 G's. Plant  
20       scale fractionation utilized a solid bowl centrifuge manufactured by Bird Machinery Company, 40 inch diameter by 60 inch bowl, typically utilized for degritting service. The speed for the plant scale machine was controlled to impart approximately 900 G's. Hydroclone  
25       equipment included two sizes of ceramically lined hydroclones, one operated with an 11" long pressure drop, 70 PSI, and the other with an 18" long pressure drop, 70 PSI.

30       The following explanation of the centrifugal acceleration appears in Perry's "Chemical Engineering Handbook," 5th Edition, Pg. 19-36.

Magnitude of Centrifugal Force. In industrial centrifuges the centrifugal acceleration is

-13-

many times the gravitational acceleration. Centrifugal force, commonly expressed in multiples of the standard force of gravity, varies with the rotational speed and with the radial distance from the center of rotation. At the wall of a bowl of diameter  $D_b$  the centrifugal force is given by

$$F_c = 0.0000142n^2D_b$$

where  $F_c$  is the centrifugal force, multiples of gravity  $n$  is the speed of rotation, r.p.m., and  $D_b$  is the bowl diameter, in.

The Ultraflotation process and products referred to in illustrative examples used a hydrosol dispersed kaolin slip containing varying amounts of soda ash from 0 to 3½#/T followed by sodium hydroxide pH adjustment, if needed, to a range between 8 and 9 is provided for the feed pulp. The hydrosol was alum-silicate based. In this operation, dispersed crude is pumped to the plant between 35 and 40% solids. After fractionation and magnetic purification, if necessary, the plant feed solids are approximately 25%. Crudes are fractionated to either 80% finer than 2 microns, 90% finer than 2 microns or 90% finer than 1 micron. The calcite carrier used in the Ultraflotation operation was ground limestone which was at least 95% -44 micron and had a surface area of 1 - 2 square meters per gram. The ground limestone was added to the pulp of dispersed fractionated kaolin clay at a concentration varying between 12 and 17% based on the weight of the kaolin, depending on the grade of kaolin being processed. Other reagents added during conditioning for Ultraflotation include: 2 - 4 pounds per ton of ammonium sulfate, 6 - 8 pounds per ton of a Tall oil/Calcium Petronate mix, 1 - 3 pounds per ton of

-14-

ammonium hydroxide, 4-6 pounds per ton of Eureka oil and 1 - 1½ pounds per ton of fuel oil. Variations in the chemical addition result from the different grades and different characteristics of the pulp to be beneficiated.

5

In carrying out the TREP process, an alum-silicate hydrosol dispersed slip generally containing no soda ash is pumped to the plant at nominally a 7.5 pH. Oxone is added to the pulp for organic contaminant control in an amount between ¼ and 1 pound per ton, depending on the level of organic contamination. Adjustments in pH within the plant are performed with sodium hydroxide as required to achieve specified ranges. The collector used is oleic acid, and the quantity added varies to satisfy the requirements of the pulp particle size distribution as received. The range is 2.5 - 3.5 pounds per ton. Examples include variations in crude particle size between 50% and approximately 70% -2 microns. As a result of the fact that there is no fractionation process upstream of the TREP, processing solids for TREP typically do not fall below 35% and may be above 50% solids. The quantity of calcium chloride added to the TREP feed during conditioning varies between .75 and 2.0 pounds per ton, depending on the soluble calcium ion content of the slip. Sodium polyacrylate dispersant (C-211) is added to optimize conditioned pulp dispersion. The quantity of C-211 added varies between 0 and 2 pounds per ton as the result of variation in slip characteristics.

30

All weights in the examples represent oxides; thus 0.5% titanium represents 0.5% TiO<sub>2</sub>.



-15-

In the examples, results from an analytical bleach procedure are reported. This is a method for determining the optimum brightness potential of a kaolin sample. The procedure removes any organic matter that may be present in the sample without using hazardous ozone by substituting potassium permanganate as the oxidant. The procedure is termed a "3/10 bleach" when the Kaolin sample is considered a "white" clay and a "5/15 bleach" when the clay is gray. The resultant bleach values when compared to the brightness obtained by conventional reductive bleaching determines the efficiency of the process to obtain the brightness potential. The procedure involves the use of excess potassium permanganate which is destroyed after the heating of the slurry by the addition of sulfur dioxide in a water solution.

#### Example 1

##### Beneficiated Kaolin Recovery from Waste Froth

Ultraflotation waste froth from a plant operated with an ultrafine particle size feed, about 90% finer than 1 micron, was evaluated using three concepts for recovery potential. These include (a) settling, (b) centrifugation alone, and (c) screening, followed by centrifugation.

In (a), froth obtained from the float plant was allowed to settle, and the kaolin layer was decanted and analyzed. The beneficiated pulp had the following analyses:

Titanium	-	.66%
Iron	-	.755%
5/15 brightness	-	90.1%

-16-

In (b), the same froth was subjected to pilot plant centrifugation. The solids of the kaolin product recovered as a centrifuge overflow was 5.0%. The centrifuged kaolin product contained .712% titanium, and  
5 had a 5/15 hot bleach potential of 90.8. As a confirmation that no other impurities were present, an LOI (loss on ignition) was checked and found to be 14.5%, indicating that essentially no carbonate remained in the recovered clay product.

10

In (c), froth was taken from the float plant, and screened through a 325 mesh Sweco screen to separate a portion of the froth. The screened froth was fed to the Sharples pilot scale solid bowl centrifuge. The  
15 beneficiated product from the froth waste had the following characteristics:

	Particle Size	- 98% - 2 microns, 90 - 1 micron
20	As recovered brightness	- 87.2%
	Iron	- .684%
	Titanium	- .773%
	3/10 brightness	- 90.0%

25 A second evaluation of (c) was completed utilizing a centrifuge feed pump setting providing three times the feed rate of the above test. The following results were obtained:

	As is brightness	- 86.9%
30	Iron	- .686
	Titanium	- .893%
	3/10 brightness potential	- 89.1%

-17-

In an additional pilot scale evaluation, similar results were obtained from a different sample of froth. The iron content was .642%, titanium .734% with a 3/10 brightness potential of 89.9.

5

### Example 2

#### Centrifuge Beneficiation of Conditioned Pulp

Conditioned but unfloated product from an Ultraflotation plant was subjected to centrifugation, utilizing a pilot plant Sharples solid bowl centrifuge. (Note that pulp obtained at this point in the process does not contain the fuel oil added for froth control.) The pulp used in this flotation operation was used to make a high brightness flotation beneficiated kaolin that is nominally 90% by weight finer than 1 micron. The following data was obtained at different settings of the positive displacement pump. (Flow is essentially proportional to the pump setting.)

20

						% by weight finer than 2 microns
25	<u>Pump Setting</u>	<u>% Solids</u>	<u>3/10 Brightness, %</u>	<u>% Titanium</u>	<u>% Iron</u>	
	4.0	22.8	90.1	.645	.666	89
	5.5	23.6	89.9	.679	.682	88
	6.5	23.6	89.7	.671	.684	88

30

As noted by the above data, a substantial amount of operational flexibility is achieved when utilizing a solid bowl centrifuge to beneficiate a conditioned product. Approximately a 50% increase in centrifuge feed

-18-

rate resulted in only a small adverse effect on final product brightness potential. Another important facet of the data is the % solids of the product from the centrifuge essentially reflects no dilution when compared  
5 to float plant feed pulp solids.

### Example 3

#### Centrifuge Beneficiation of Conditioned Pulp

10       Conditioned pulp samples were obtained from the Ultraflotation plant and subjected to centrifugation. The same type of kaolin used in Example 1 was employed. Results of Ultraflotation and the process of the invention were compared.

15

The attached table reflects the results of the pilot scale evaluations. Note the differential in total plant TMD (total machine discharge) solids vs. the solids obtained by the new beneficiation method. Also note  
20 centrifuge conditions were varied in order to beneficiate as well as fractionate the final products between 80% and 90% finer than 2 microns. Samples subjected to the centrifuge beneficiation during one trial represent a 90% finer than 2 microns plant product (See Table 1).  
25 Included is a typical analysis, done by atomic absorption, of centrifuge processed product and the

-19-

resulting underflow (impurity + carrier) from the process  
(See Table 2).

A sulfuric acid titration to quantify the residual  
5 calcite carrier in the centrifuge product vs. plant  
processed grade yielded a titre of .232 grams vs. .234  
grams. This demonstrated essentially complete separation  
of carrier. In order to identify the impact on product  
viscosity, plant processed vs. centrifuge processed  
10 product from the same feed pulp were evaluated by the  
known Brookfield (BF) and Heliopath (HEP) procedures (See  
Table 3)..

-20-

Table 1

## 5 Results of Bird Centrifugation of Conditioner Product

	<u>Solids</u>	<u>PSD</u> <u>@ 2</u>	<u>TMD</u>	<u>%</u> <u>Brightness</u>	<u>%</u> <u>TiO2</u>	<u>%</u> <u>Fe</u>	<u>Product</u>
10	18.8	80	86.4	90.0	.510	.687	Control**
	22.8	89	86.8	90.4	.525	.686	PS-4
15	23.6	86	86.9	90.5	.514	.696	PS-5
	25.2	82	86.7	90.0	.530	.669	PS-7
	22.5	90	86.7	90.0	.538	.687	PS-4
20	23.8	86	86.7	90.0	.524	.706	PS-5
	25.2	81	86.7	90.1	.520	.661	PS-7
25	24.4	91	86.7	90.4	.629	.682	PS-4
	24.9	91	86.8	90.5	.617	.697	PS-5
30	17.3	90	86.7	90.4	.630	.701	Control

PS = Pump Setting

-21-

Table 2

5		<u>Bird Centrifuge Kaolin Product</u>	<u>Bird Centrifuge Underflow Product</u>
		<u>Wt., %</u>	<u>Wt., %</u>
	Kaolin	98.6	21.40
	CaCO <sub>3</sub>	0.21	69.04
10	TiO <sub>2</sub>	0.41	9.07
	Fe <sub>2</sub> O <sub>3</sub>	0.62	0.48

Table 3

15		<u>% Solids</u>	<u>pH</u>	<u>BF</u>	<u>HEP</u>	<u>PSD @ 2 Microns</u>
	Control	70.0	6.5	222	1100/5.0	89
20	Centrifuged Product	70.0	6.6	262	1100/4.2	91
25	No detrimental effect on viscosity is indicated from the above data.					

-22-

Example 4Centrifuge Beneficiation of Conditioned Pulps  
(Ultraflotation)

5

Two commercial Ultraflotation plants were provided a common ultrafine impure kaolin feed. The beneficiation of the feed, utilizing one of the float plants performing at steady state conditions, established the control for the full scale experiment. The conditioned product from the other float plant was directed to a commercial 40 x 60 Bird solid bowl centrifuge for the purpose of comparing the two processes. The following results were obtained.

15

	<u>Bright</u> <u>3/10</u>	<u>TMD</u>	<u>Titanium,</u> <u>%</u>	<u>Iron</u> <u>%</u>
20 Control	90.2	86.9	.629	.838
25 #4 Bird Product	90.4	87.1	.633	.899
#5 Bird Product	90.6	87.5	.627	.899



-23-

Example 5Hydroclone Beneficiation of Conditioned Pulp

Two different sizes of cyclones were utilized to evaluate the potential of beneficiation at a lower level of G's. The control for the experiment was the performance of the same pulp beneficiated using plant froth flotation. The following results were obtained:

	<u>% TMD</u>	<u>3/10</u>	<u>%</u>	<u>%</u>
	<u>Brightness</u>	<u>B1 BR</u>	<u>Titanium</u>	<u>Iron</u>
Control	86.8	90.3	.560	.674
Small Cyclone	87.2	90.3	.574	.663
Large Cyclone	86.7	90.3	.581	.663

Example 6Centrifugal Beneficiation of TREP Conditioned Pulp

A TREP conditioned whole fraction kaolin crude having a particle size distribution of 61 $\pm$ 2 microns at nominally 35% solids was used to feed the pilot plant Sharples centrifuge to demonstrate the centrifuge beneficiation process and to achieve simultaneous fractionation to a #1 coating clay fraction. Conditioning for TREP was carried out using a squirrel cage conditioner. The following results were obtained:

	<u>% GE</u>	<u>%</u>	<u>%</u>
	<u>Brightness</u>	<u>Titanium</u>	<u>Iron</u>
TREP Plant Feed	82.4	.45	0.3
Beneficiated & Fractionated Product	86.1	.73	.25

Final product characteristics 94-2u reduction bleached brightness potential was 89.4% at 10# bleach.

-24-

Example 7Ultraflotation Carrier Reuse

5 A laboratory study was initiated to identify the potential for recycling carrier isolated in the centrifuge beneficiation process. All the experiments utilized a total carrier loading of 15%.

10 With 100% fresh limestone, full reagent addition was practiced. With recycled limestone, an additional benefit was identified in that only 80 - 90% of the anticipated flotation reagents had to be added. This suggests that used carrier maintained an effective level of collector at an activity suitable to further  
15 beneficiate kaolin. Carrier reuse will provide cost reduction in both carrier and reagent cost. The following results were obtained:

		% <u>TMD Brt</u>	% <u>3/10 Brt</u>	% <u>Titanium</u>	% <u>Iron</u>
20	Experiment A				
	Control	87.1	90.3	.552	.691
	Recycled Limestone	86.6	89.9	.693	.714
25	Experiment B				
	Control	86.8	89.8	.602	.676
30	Recycled Limestone	87.9	89.6	.591	.672
	Experiment C				
35	Control	86.5	90.2	.604	.709
	Recycled Limestone	86.8	90.2	.658	.764

40 NOTE: All recycle experiments had 10% fresh and 5% recycled material.

-25-

It is anticipated that by practice of the process of the invention, beneficiating without utilizing the Denver flotation cells and other equipment should approach 300 horsepower or approximately 7.5 horsepower hours per ton of product.

5

-26-

We claim:

1. A method for treating an aqueous pulp containing dispersed kaolin clay particles and nonkaolin particles including impurities that are coated with an anionic collector reagent which comprises subjecting said pulp to the action of gravitational forces by centrifugation or hydrocloning using sufficient force to sediment selectively said collector-coated nonkaolin particles including impurities and separating said sediments from the remainder of the pulp which is a dispersed concentrate of kaolin particles.
2. The process of claim 1 wherein said aqueous pulp is a waste froth product obtained by anionic flotation of impure kaolin and is a concentrate of impurities therein.
3. The process of claim 1 wherein said waste product is obtained by Ultraflotation of impure kaolin and the sediment included collector-coated carrier material used in Ultraflotation.
4. The process of claim 1 wherein said waste product is obtained by froth flotation of impure kaolin using collector-coated calcite carrier and the sediment includes collector coated calcite.
5. The process of claims 3 and 4 wherein said sediment which contains collector coated carrier is recovered and used as a collector in a subsequent froth flotation process.

-27-

6. The process of claim 1 wherein said collector comprises a fatty acid.

5 7. The process of claim 1 wherein said impurities comprises iron-bearing titania.

8. The process of claim 1 wherein said aqueous pulp containing said dispersed kaolin clay particles and said non-kaolin particles including  
10 impurities is obtained by dispersing an impure kaolin clay in water, conditioning said pulp with an anionic collector reagent selective to impurities in said clay, and said gravity separation step is carried out without an intermediate froth flotation step.

15

9. The process of claim 8 wherein a carrier mineral is added to said pulp during conditioning and said anionic reagent is also selective to said carrier mineral.

20

10. The process of claim 9 wherein said carrier mineral is calcite and said anionic collector comprises a fatty acid.

25

11. The process of claim 8 wherein said collector comprises oleic acid and a water soluble calcium salt is also added during conditioning.


12. The process of claim 1 wherein a  
30 centrifuge is used.

13. The process of claim 1 wherein a hydroclone is used.

## INTERNATIONAL SEARCH REPORT

PCT/US 92/05182

International Application No

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5	B03B1/04; C04B33/04;	B03D1/12; B28C1/08
		B03D1/02; B03B9/00
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	B03B ; B03D ; B28C	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X Y	US,A,3 425 546 (B. DUKE) 4 February 1969 see column 1, line 43 - column 2, line 3  see column 3, line 36 - line 50 see column 4, line 11 - line 50 ---	1-7 9,10,12, 13
X Y	US,A,3 253-791 (I. COHN) 31 May 1966 see column 5, line 24 - line 58  see column 7, line 3 - line 33 see column 7, line 67 - column 8, line 54 ---	1,8 9,10,12, 13
A	EP,A,0 104 099 (ENGELHARD CORPORATION) 28 March 1984 see page 11, line 36 - page 12, line 36 & US,A,4 472 271 18 September 1984 cited in the application ---	11
A		
	---	
	---/---	
<p><sup>10</sup> Special categories of cited documents : <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
02 SEPTEMBER 1992	02. 10. 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	LAVAL J.C.A. 	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	US,A,2 990 958 (W. GREENE) 4 July 1961 cited in the application ---	
A	US,A,4 014 709 (R. DYKSTRA) 29 March 1977 cited in the application ---	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO. US 9205182  
SA 61697**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 02/09/92

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-3425546	04-02-69	None	
US-A-3253791		None	
EP-A-0104099	28-03-84	US-A- 4472271	18-09-84
		AU-B- 567110	12-11-87
		AU-A- 1836683	01-03-84
		DE-A- 3382582	23-07-92
US-A-4472271	18-09-84	AU-B- 567110	12-11-87
		AU-A- 1836683	01-03-84
		DE-A- 3382582	23-07-92
		EP-A, B 0104099	28-03-84
US-A-2990958		None	
US-A-4014709	29-03-77	None	